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The Laser Raman Spectrum of Poly(ethylene Glycol Dimethacrylate)

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ABSTRACT

The laser Raman spectrum of poly(ethylene glycol dimethacrylate) (PEGDMA) with depolarization data is presented. Qualitative vibrational assignments of the observed bands are proposed using the empirical method of characteristic group frequencies.

INTRODUCTION

The laser Raman spectrum of poly(ethylene glycol dimethacrylate) (PEGDMA) with depolarization results is reported. The vibrational assignments were accomplished by using characteristic group frequencies and by comparison with the infrared and Raman spectra of other methacrylates such as poly(methyl methacrylate) (PMMA) [1] and other esters [2-4].

The laser spectrum of PEGDMA is shown in Fig. 1. The bands of the infrared [5] and the Raman spectra of PEGDMA are listed in Table 1 with the relative intensities and the perpendicular depolarization ratios (ρ_{\perp}) of the Raman bands. The intensity distribution in the two types of spectra differ in that the most prominent bands in one spectrum are almost invariably weak in the other. Analysis

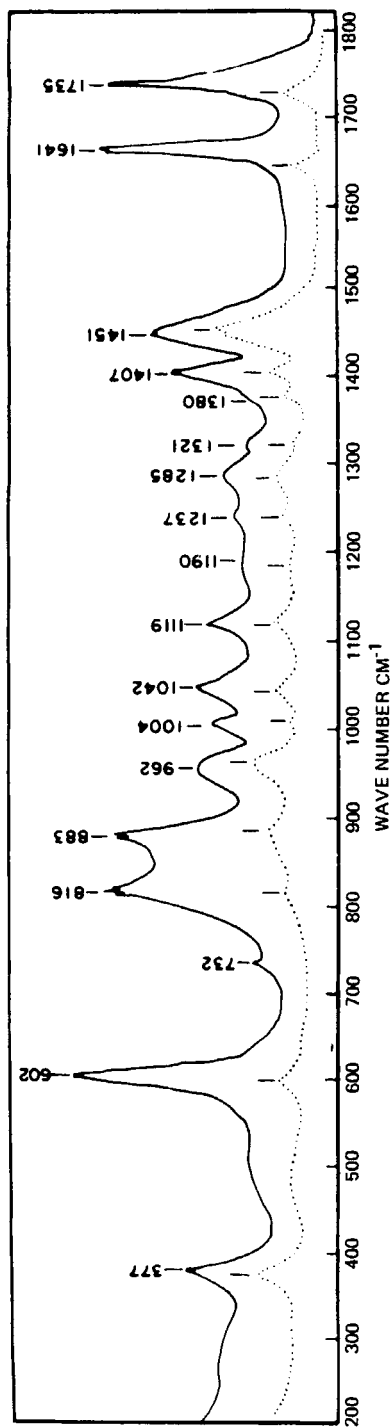


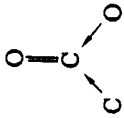
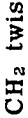
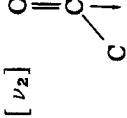
FIG. 1. Raman spectrum of poly(ethylene glycol dimethacrylate). Solid line: Analyzer transmitting only light polarized parallel to incident laser beam. Dotted line: Analyzer transmitting only light polarized perpendicular to incident laser beam.

TABLE 1^a

Observed infrared frequency (cm ⁻¹) [5]	Observed Raman frequency (cm ⁻¹)	Relative Raman intensities at 0° polarization	Relative Raman intensities at 90° polarization	Perpendicular depolarization ratios (ρ_{\perp})	Vibrational assignment
-	377	25	18	0.72	$[\nu_3]$ (δ_s in plane)
-	602	50	13	0.26	ν_s (C-C O)
-	732	11	-	-	ν (C-C) skeletal mode
810	816	43	12	0.28	ν_s (C-O-C)
885	883	41	16	0.39	CH ₂ (rock)
942	962	24	18	0.75	α -CH ₃ (rock)
1010	1004	20	10	0.50	-
1042	1042	22	19	0.86	ν (C-C) skeletal mode
-	1119	21	14	0.67	ν (C-C) skeletal mode
1149	-	-	-	-	-
1186	1190	14	10	0.71	ν_a (C-O-C)

(continued)

TABLE 1 (continued)

Observed infrared frequency (cm ⁻¹) [5]	Relative Raman intensities at 0° polarization	Relative Raman intensities at 90° polarization	Perpendicular depolarization ratios (ρ_{\perp})	Vibrational assignment
1242	16	12	0.75	on (C-O) stretch 
1285	18	15	0.83	
1316	13	9	0.69	δ_s (C-H) of α -(CH ₃) 
1372	14	9	0.83	
1404	27	15	0.56	CH ₂ twist or wag
1439	-	-	-	-
1449	33	26	0.75	δ_a (C-H) of α -(CH ₃)
1645	43	10	0.23	(C=C) stretch 
1727	45	11	0.24	[ν_2] O=C=O, (ν_s) C=O
2950	-	-	-	

ν = stretching, δ = deformation, s = symmetric, a = asymmetric.

of the PEGDMA spectrum and a comparison to a similar analysis for PMMA [1] suggests that this occurs because the asymmetric stretching modes of the ester group are strong in the infrared and weak in the Raman spectra while the converse is true for the corresponding symmetric stretching modes. Bands which are attributed primarily to C-C stretching and deformation of the polymer backbone are medium-to-weak in intensity in both the infrared and the Raman spectra.

EXPERIMENTAL

Polymer samples in the form of flat sheets were obtained by the photopolymerization of ethylene glycol dimethacrylate (EGDMA) with benzoin (0.1 wt%) as a photoinitiator. The polymerization was conducted by exposing the mixture to ultraviolet radiation (365 nm) for 48 h. Unreacted monomer (less than 0.5% of the polymer sheet) was removed by heating the polymer in a vacuum oven.

The Raman spectra were obtained by excitation of the polymer sample with a Spectra Physics 166 argon-ion laser. Frequency scanning was done by a Spex 1401 double monochromator equipped with a photon counting detection system consisting of a RCA 31035 photomultiplier tube in connection with a Princeton Applied Research Corp. Model 1112 photon counter/processor and a Model 1120 amplifier/discriminator. The laser was operated at 514.5 nm with approximately 200 mW of power at the sample. In all cases the slit width was 200 μm and the scanning rate was 1 cm^{-1}/s with a time constant of 2 s. All spectra were calibrated against a spectrum of CCl_4 for wavenumber accuracy.

Clear pellet transmissions were obtained with a focused laser beam. No fluorescence or thermal degradation was observed for these measurements; therefore, no sample preparation was necessary.

The perpendicular depolarization ratios (ρ_{\perp}) were measured by the use of a quartz wedge polarization scrambler fitted on the entrance slit of the monochromator. The two components of polarization were separated with a polaroid plate in the collimation light space of the input optics.

The relative band intensities were measured as band areas by the use of a Keuffel & Esser Model 620005 Compensating Polar Planimeter.

RESULTS AND DISCUSSION

C-H Deformations in the 1500 to 1300 cm^{-1} Region

The Raman spectrum for PEGDMA has a strong feature at $\Delta\nu = 1451 \text{ cm}^{-1}$ (depolarized) and weaker bands at $\Delta\nu = 1407$ and 1380 cm^{-1} .

The weak Raman band at $\Delta\nu = 1407 \text{ cm}^{-1}$ has an equivalent infrared band at 1404 cm^{-1} . This suggests its assignment to a CH_2 wagging or twisting mode while the Raman band at $\Delta\nu = 1451 \text{ cm}^{-1}$ is equivalent to the 1449 cm^{-1} infrared band and has been assigned as the asymmetric deformation $\delta_a (\alpha\text{-CH}_3)$. This is in the frequency range of 1470 to 1444 cm^{-1} assigned by Sheppard and Simpson [6] as typical for deformations of an isolated methyl group on a carbon skeleton.

The infrared spectrum of PMMA has bands occurring at 1438 and 1388 cm^{-1} which have no equivalent in the Raman spectrum of PMMA. These were assigned by Nagai [7] as the symmetric deformation $\delta_s (\text{O-CH}_3)$ and $\delta_s (\alpha\text{-CH}_3)$, respectively. It was suggested by Jones [8] that the absence of these bands in the Raman spectrum confirms this assignment since the symmetrical methyl deformation mode is usually missing or very weak in the Raman spectra of unsaturated hydrocarbons. In PEGDMA, there is a Raman band at $\Delta\nu = 1380 \text{ cm}^{-1}$ which can be assigned to the $\delta_s (\text{C-H})$ of $\alpha\text{-CH}_3$.

The Carboxyl Group

One or more very strong infrared adsorption bands between 1600 and 1800 cm^{-1} can be used to identify carboxyl compounds. These bands are somewhat less strong in the Raman effect and may appear at different positions from the infrared if more than one carboxyl group is present [9]. The type of carboxyl present may be indicated by the position and contours of the C=O stretching bands. Aldehydes usually have weak infrared bands near 2700 cm^{-1} while saturated open chain ketones have bands between 1700 and 1725 cm^{-1} . Carboxylic acids have strong, multiple infrared and Raman bands in the $1600\text{-}1800 \text{ cm}^{-1}$ region which tend to coincide in the two spectra but with different intensity patterns [9]. In esters, one or two strong bands in the $1720\text{-}1800 \text{ cm}^{-1}$ region and a pair of medium-to-strong bands, one at $1000\text{-}1100 \text{ cm}^{-1}$ and the other at $1100\text{-}1300 \text{ cm}^{-1}$, appear. Tobin [9] indicated that the bands near 1700 cm^{-1} and between $1100\text{-}1300 \text{ cm}^{-1}$ are strong in the infrared spectrum and the band between $1000\text{-}1100 \text{ cm}^{-1}$ is strong in the Raman spectrum. Cornish and Davison [10] showed that the C=O frequencies of methyl esters are higher than other esters for even-numbered dicarboxylic esters. All compounds with a saturated carbon atom adjacent to the carboxyl group absorb at $1720\text{-}1730 \text{ cm}^{-1}$ with the exception of methyl acetate which absorbs at a higher position. Davison and Bates [3] suggested that, whereas acrylates absorb at $1717 \pm 3 \text{ cm}^{-1}$, α - or β -Methyl substitution of the double band, as in crotonates and methacrylates, lowers the frequency to $1708\text{-}1710 \text{ cm}^{-1}$.

With PMMA, Haverillak and Roman [11] assigned the strong pair of infrared bands (1190 and 1150 cm^{-1}) as ester bands and Willis [1] assigned the corresponding Raman bands at $\nu_a (\text{C-O-C})$, the asymmetric carboxyl stretch. In PEGDMA, similar infrared bands at

1149 and 1186 cm^{-1} are observed; the latter band corresponds to a Raman band at $\Delta\nu = 1190 \text{ cm}^{-1}$.

The symmetrical stretch ν_s (C-O-C), appearing as a strong, polarized band of PMMA at $\Delta\nu = 818 \text{ cm}^{-1}$ and at $\Delta\nu = 830 \text{ cm}^{-1}$ in methyl methacrylate monomer [3], suggests that the Raman band occurring at $\Delta\nu = 816 \text{ cm}^{-1}$ in PEGDMA is due to this mode.

The C=C Stretching Band

Values for the positions and intensities of the C=C stretching bands given by Davison and Bates [3] for acrylates are 1638 ± 2 and $1622 \pm 2 \text{ cm}^{-1}$ and for methacrylates as $1637 \pm 3 \text{ cm}^{-1}$. Further examples are presented by Katritzky et al. [2]. Hence the polarized Raman band at $\Delta\nu = 1641 \text{ cm}^{-1}$ for PEGDMA and its corresponding infrared band at 1645 cm^{-1} can be assigned to the C=C stretching mode. This Raman band is particularly significant since it can be related to the efficiency of cross-linking in the polymer network [12].

Other Bands in PEGDMA

Bands occurring in the Raman spectrum of PEGDMA at $\Delta\nu = 1042$ and 1199 cm^{-1} have been assigned to the (C-C) skeletal mode. The corresponding infrared band at 1042 cm^{-1} is observed. However, a very broad band due to the (C-O) stretch occurs in the infrared spectrum between $1100\text{-}1200 \text{ cm}^{-1}$. Willis [1], by means of computer analysis, was able to resolve the 1300 to 1050 cm^{-1} region for PMMA into a series of Lorentzian bands. This revealed a band at 1125 cm^{-1} which was assigned as a skeletal mode, either a pure C-C stretch [13] or a combination of CH_3 (rock), CH_2 (wag), and C-C stretch [14]. This suggests that the $\Delta\nu = 1119 \text{ cm}^{-1}$ band for PEGDMA is also due to this mode.

Nagai [7] and Haveriliak and Roman [11] have assigned the 1063 cm^{-1} band of PMMA as a backbone mode. This indicates that the Raman band for PEGDMA at $\Delta\nu = 1042 \text{ cm}^{-1}$ is also a backbone mode. Katritzky et al. [2] proposed the assignment for the 970 cm^{-1} infrared band and the $\Delta\nu = 967 \text{ cm}^{-1}$ Raman band for PMMA as the (α - CH_3) rocking mode. This corresponds to the depolarized Raman band at $\Delta\nu = 962 \text{ cm}^{-1}$ and the 970 cm^{-1} infrared band in PEGDMA.

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